

TELECHELIC EMISSIVE OLIGOMERS AND POLYMERS DERIVED THEREFROM

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention is directed to telechelic emissive, semi-conductive end-functionalized oligomers which can be polymerized by a variety of conventional techniques to afford emissive polymers. The polymers are useful as active layers in light emitting as well as photovoltaic devices.

Discussion of the Art

[0002] Polyphenylenes, polyfluorenes and other conjugated aromatic polymers are well known as active layers in electroluminescent devices. See U. Scherf and E.J. List, *Adv. Mater.*, 14 (7), 477 (2002), and M.T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 12 (23), 1737 (2000). These polymeric materials are generally prepared using aromatic coupling reactions, such as the Suzuki or Stille coupling or the nickel catalyzed coupling reactions of aryl halides. Although the methodology for preparing these polymers has been well established, in many cases the coupling-polymerization reactions afford by-products that limit the molecular weight and may either quench fluorescence or induce significant red shifts in the emission spectrum, thus limiting the color tunability of the devices.

[0003] Electroluminescent polymers bearing linking groups have been prepared and converted to electroactive copolymers by various methods. See C. Schmitt, H.G. Nothofer, A. Falcou and U. Scherf, *Macromol. Rapid Commun.*, 22, 624 (2001); T. Miteva, A. Meisel, W. Knoll, H.G. Nothofer, U. Scherf, D.C. Muller, K. Meerholz, A. Yasuda and D. Neher, *Adv. Mater.*, 13 (8), 565 (2001); and R. Friend, J. Burroughs and D. Bradley, U.S. Patent No. 5,427,190 (1993) issued to Cambridge Display Technologies. The polymers in this invention are derived from phenol, thiophenol or aryl amine end-functional oligomers that can be converted into a variety of copolymers via these

functional moieties. The oligomers or copolymers prepared according to the methods described are not believed to be known in the existing art.

BRIEF SUMMARY OF THE INVENTION

[0004] In accordance with a first aspect of the invention, a process to prepare end-functionalized conjugated oligomers of polyarylenes that can be polymerized via the reactive end-group is provided.

[0005] A further aspect of the invention relates to the reaction of a phenol, thiol or amine functional moiety, which is substituted with either an aryl halide or an aryl boronic acid or ester, with either a bis-boronic acid or ester or a bis-haloarene using Suzuki coupling conditions to form the end-functionalized conjugated oligomers of polyarylenes.

[0006] Another aspect of the invention relates to polymerization of the end-functionalized conjugated oligomers of polyarylenes prepared according to the invention by reacting the phenol, thiol or amine functional moiety of the oligomer with a difunctional monomer to form the polymer.

[0007] An additional aspect of the invention relates to the telechelic emissive, semi-conductive end-functionalized oligomers and polymers produced therefrom.

[0008] A further aspect of the invention relates to the use of the emissive polymers of the invention in the formation of films for use in, for example, light emitting and photovoltaic devices.

[0009] These and other aspects and objects of the invention will become apparent upon reading and understanding of the detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[00010] The invention may take form in various components and arrangements of components, and in various steps and arrangement of steps. The drawings, in which like

reference numerals denote like components through the views, are only for purpose of illustrating particular embodiments and are not to be construed as limiting the invention.

[00011] The Figure illustrates, in a schematic format, one embodiment of a process for preparing the oligomers and corresponding polymers of the invention.

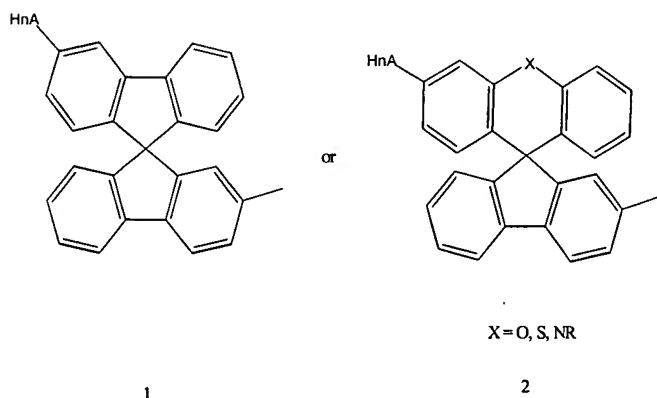
DETAILED DESCRIPTION OF THE INVENTION

[00012] The present invention is directed to a family of telechelic oligomers, polymers derived from them, and to an efficient process to prepare end-functionalized conjugated oligomers. There are a number of advantages to the approach described in this disclosure. For example, the telechelic oligomers can be readily purified by conventional techniques (chromatography, recrystallization, etc.). Also, the emissive components of the oligomers can be readily varied to achieve desirable processability characteristics, color emission, emission efficiency and charge transport properties. Further, the conjugation length is readily tailored and the polymerization chemistry can be selected to minimize side reactions, maximize molecular weight control and tailor physical properties of the final polymer.

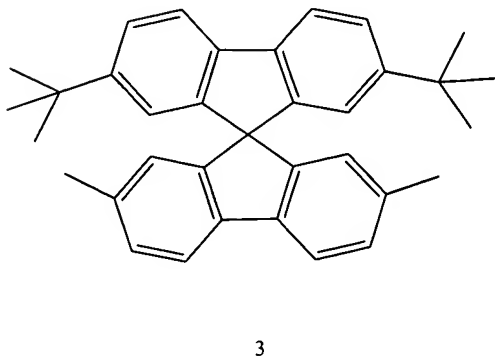
[00013] The oligomers of the invention are prepared by reaction of a phenol, thiophenol or amine functional moiety, appropriately substituted with either an aryl halide or an aryl boronic acid or ester, with either a bis-boronic acid or ester or a bis-haloarene respectively using Suzuki coupling conditions as described in N. Miyaura, T. Yanagi and A. Suzuki, *Synth. Commun.*, (11) 513, (1981). The resulting oligomers can then be purified using conventional techniques. The purified oligomers may then be polymerized by reactions of the phenol, thiol or amine functional group with appropriate co-monomers to afford, for example, polycarbonates, polyesters, polyethers, polysilylethers, polyetherimides, polyimides. The resulting polymers can be isolated and fabricated into films or other media suitable for construction of devices such as light emitting devices and photovoltaic devices.

[00014] Additionally, the present invention is directed to polymers, and active layers of certain devices, such as light emitting devices, or photovoltaic devices, that are prepared from the process of the invention.

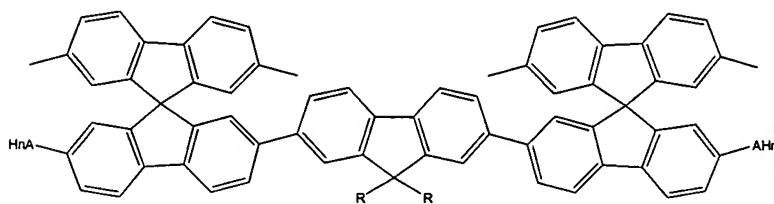
[00015] A schematic example of this concept is illustrated in the Figure. In this scheme, Ar represents any aromatic moiety including, but not limited to phenyl, substituted phenyl, naphthyl, anthryl, biphenyl, etc., and any substituted variants of these species. “A” can be oxygen, sulfur or nitrogen, “n” is 1 or 2 depending on A. R may be, independently, alkyl, branched alkyl, hydrocarbon chains having 1 to about 40 carbon atoms, alkyl chains substituted with fluorine, cyano or aryl groups, aryl or substituted aryl. Additionally, Ar and the aryl ring bearing the AH_n may be connected to each other by a carbon or carbon-heteroatom bond, such as in structures 1 and 2.



[00016] Likewise, the R groups may be linked together as in structure 3.

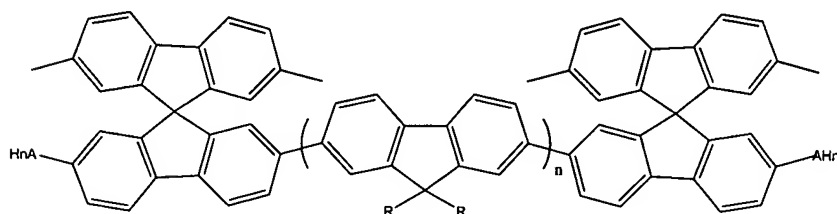


[00017] The AHn functional group used for linking these oligomers together may also be attached to other portions in this oligomer, such as in structure 4.



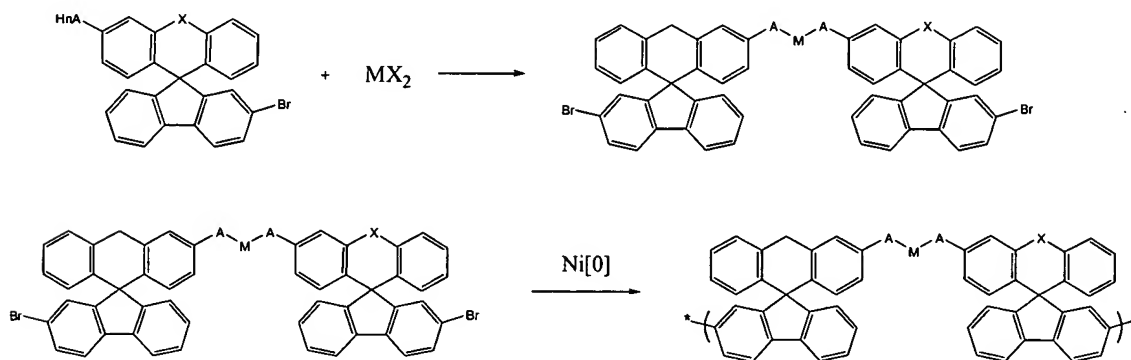
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[00018] Additionally, the oligomer length can be extended as in the generic structure 5.



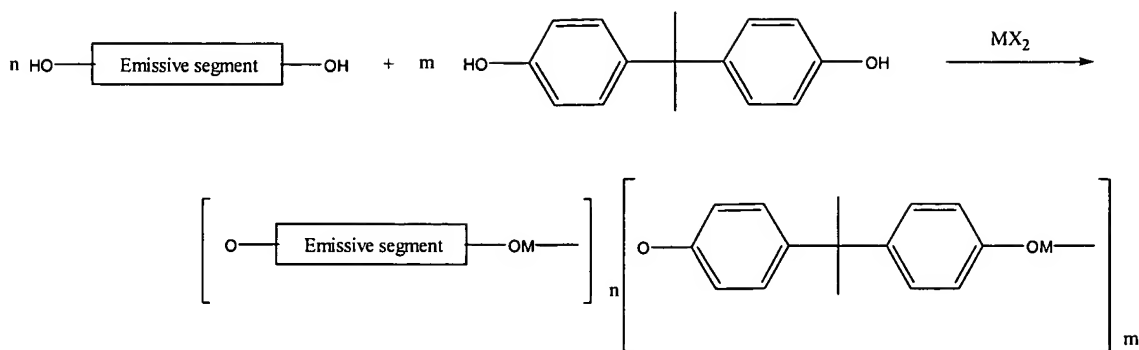
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[00019] Further, some of the polymers described herein may also be obtained by first linking the AHn functional components together via a carbonate, or other suitable linkage, and then polymerizing through the arylhalide function using typical aryl coupling chemistry, such as described by Suzuki or Yamamoto previously referenced herein. Such a method would essentially be a reversal of the order of events to obtain the desired materials. This process is shown in the following scheme:

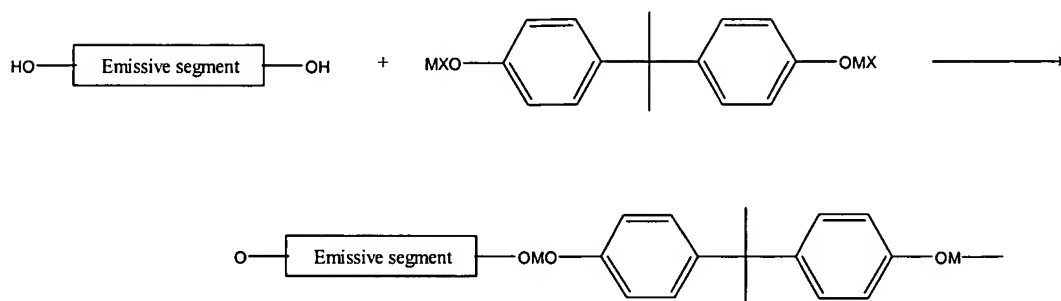


[00020] MX_2 is any difunctional monomer capable of reacting with AH_n to form a homopolymer or copolymer. Examples of MX_2 include but are not limited to BPA-bis-chloroformate, terephthalic acid or its diacid chloride, dichlorophenylsulfone, pyromellitic dianhydride, adipoylchloride, diphenyldichlorosilane, dimethyldichlorosilane, 1,1,3,3-tetramethyldisiloxane, phosgene and the like, and mixtures thereof.

[00021] The “homopolymer” in this context means that the emissive segments are linked together solely by the linker MX_2 . See, for example, structure 6. The “copolymer” in this context refers to structures wherein one or more emissive segments and/or a non-emissive segments are linked together by the link MX_2 . The link segments in a copolymer can be dispersed randomly or in an alternating manner. The latter is referred to as an alternating copolymer, which is often abbreviated “alt-w-polymer.” Structures 6 and 7 are illustrative of these types of structures:



6 "random" copolymer



7 "alt-copolymer

[00022] In the schematic shown in the Figure, the starting material, a halogenated fluorenone such as 2-bromo-fluorenone (Ia), can be prepared by known procedures such as that described in J. Chem. Soc., p 1737, (1970) and by direct bromination of fluorenone in the presence of Fe and methylene chloride. Halogenation may take place at more than one position on the fluorenone ring system as in, for example, 2,7-dibromo-fluorenone.

[00023] The halogenated fluorenone (Ia) is then converted into intermediate reaction product (Ib) via a Grignard reaction. In the schematic shown in the Figure, a Grignard reactant ArMgX where Ar represents any aromatic moiety including, but not limited to, phenyl, substituted phenyl, maphthyl, anthryl, biphenyl, etc. and any substituted variants thereof, and X is halogen, is reacted with the halogenated fluorenone (Ia) to produce an intermediate reaction product, such as the carbinol of formula (Ib) as shown in the Figure.

[00024] The carbinol of formula (Ib) is then reacted with a phenol, thiol or amine functional moiety. In the scheme of the Figure, the carbinol is reacted with a phenyl ring having OH, SH, or NH₃ attached thereto which forms the compound of formula (Ic). While the compound (Ic) in the Figure has an aryl halide substitution, this derivative may be converted to an aryl boronic acid or ester prior to the coupling step.

[00025] The compound of formula (Ic) is then reacted with either a bis-boronic acid or ester or a bis-haloarene under conventional Suzuki coupling conditions as mentioned hereinbefore. In the reaction scheme of the Figure, a bis-boronic acid of Formula (Id) is reacted with the compound of Formula (Ic) in the presence of (Ph₃P)₄, K₂CO₃ and toluene to form the oligomer of Formula (Ie)

[00026] The oligomer of Formula (Ie) can then be polymerized by reacting the phenol, thiol or amine functional moiety with an appropriate co-monomer (difunctional monomer). The comonomer as shown in the reaction scheme of the Figure has a formula MX₂ and is for example, phosgene. As shown in the Figure, the resultant polymer is a compound of Formula (If).

[00027] In one embodiment a polymer of the general formula:



is formed in accordance with the present invention. D is preferably an "A-functional" segment of the general formula:



wherein Ar is an aromatic unit selected from the group consisting of phenyl, substituted phenyl, naphthyl, anthryl, biphenyl, substituted variants thereof, and mixtures thereof; A is selected from the group consisting of oxygen, nitrogen, sulfur, nil, and mixtures thereof; wherein "nil" represents a conjugation length of (D-G_n-G) that is interrupted by the A-M linkage and is an integer between about 1 and 3; G is preferably an oligophenylene, such as oligofluorene, as previously described; n is preferably an integer between about 1 and about 25, M is a linking group formed by reacting the emissive

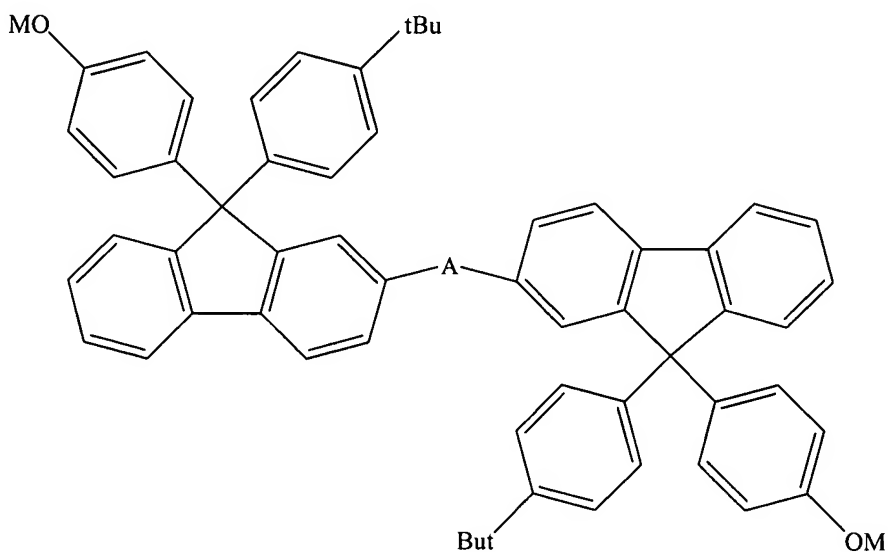
segment with a MX_2 linker as previously described, and m is an integer between about 1 and about 1000.

[00028] The following examples are meant for illustrative purposes only and are not intended to limited the invention to the particular embodiments described therein:

EXAMPLES

Example 1: Preparation of coumpound 1(f) from the Figure where $\text{R} = \text{n-hexyl}$, $\text{Ar} = 4\text{-t-butylphenyl}$, $\text{A} = \text{O}$ and $\text{MX}_2 = \text{phosgene}$

[00029] A Grignard reagent prepared from 4.47 g. (21 mmol) of 4-t-butylbromobenzene and 0.753 g. (31 g-atoms) of magnesium plus 10 mmol of 1,2-dibromoethane in 50 ml of ether was treated over one hour with a hot solution of 5.18 g. (20 mmol) of 2-bromofluorenone in 25 ml. of toluene. The mixture was refluxed for one hour then quenched by addition of 50 ml. of saturated aqueous ammonium chloride. After separation and washing of the organic layer, solvent was evaporated to yield 10 g. of an oil that was chromatographed on 50 g. of silica gel (20% ethyl acetate-hexane as eluant). The product was a carbinol which was then isolated as an off-white solid in 92% yield. Reaction of this carbinol, (15.5 mmol) with 1.5 equivalents of phenol in methylene chloride (10 ml.) in the presence of

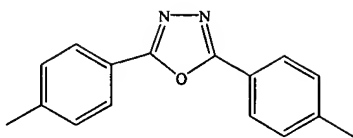


methanesulfonic acid (200 μ l) afforded 2-bromo-9-(4-t-butylphenyl)-9-(4-hydroxyphenyl)fluorene (61%) yield. Reaction of the 2-bromo-9-(4-t-butylphenyl)-9-(4-hydroxyphenyl)fluorene compound with 0.5 equivalents of 9,9-dihexyl-2,7-bis-trimethyleneborate in a toluene/2M K₂CO₃ mixture in the presence of hexaethylguanidinium chloride (1mol%) and tetrakis-triphenylphosphine palladium(0) (1.6mol%) afforded the terfluorene bisphenol (68% yield). Mass spectrum: m/e 1110 (M⁺). Reaction of this bis-phenol with one equivalent of phosgene in methylene chloride in the presence of a pH 10 buffer afforded approximately an 80% yield of polymer 1(2) gpc (PS standards) Mw = 25025; Mn = 7808 Mw/Mn = 2.96.

[00030] Other functional monomers and polymers have been prepared using procedures similar to that described above. A summary of pertinent data for these materials is presented in Table 1.

[00031] Table 1. Pertinent data for oligomers and polymers

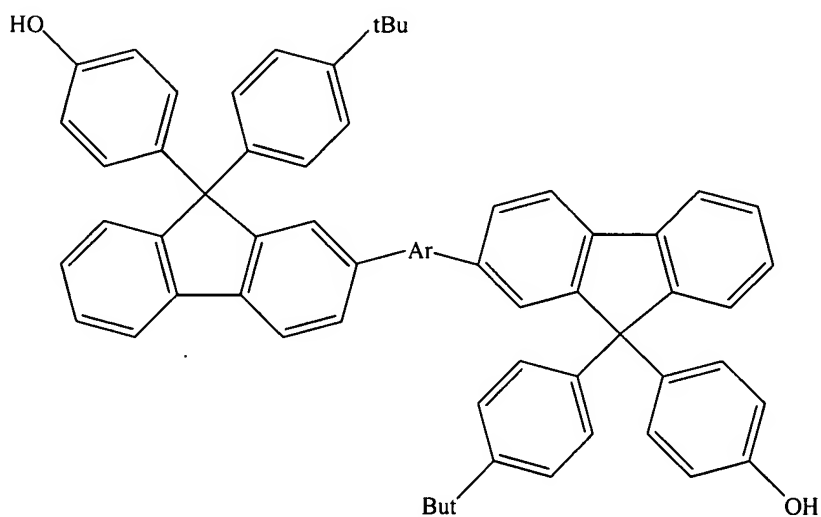
A	M	Mw	Mn	Mw/Mn	Uv(max)	Emm(max)
9,9-dihexylfluorene-2,7-diyl	H	1,110	1,110	1.00	350	400, 425
9,9-dihexylfluorene-2,7-diyl	CO	43,237	15,014	2.88	350	400, 425
9,9-dihexylfluorene-2,7-diyl	CO/ (OBPAOCO)	35,818	15,273	2.34	350	400, 425
9,9-dihexylfluorene-2,7-diyl	COOBPAOCO	20,098	8464	2.37	354	
9,9-dihexylfluorene-2,7-diyl	Ph ₂ Si	<15,000	<5,000	-	-	
---	H	778	778	1.00	334	
---	COOBPAOCO	42,917	9307	4.61	333	
Oxa ^a	H	998	998	1.00	347	
Oxa ^a	COOBPAOCO	28,547	12,309	2.32		
9,10-anthryl	H	954	954	1.00	382, 407	
9,10-anthryl	COOBPAOCO	31,942	13,420	2.38	383, 399	



a=

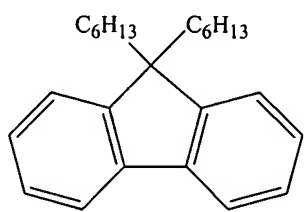
[00032] In addition to the above, the following tables 2 and 3 illustrate other monomeric and polymeric structures of compounds within the scope of the invention, a number of physical properties associated with the monomers and polymers are also represented in the tables below.

[00033] Table 2. Monomers

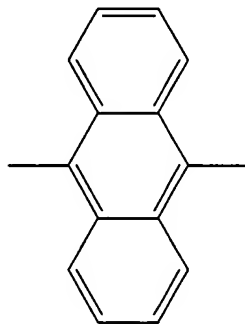


[00034]

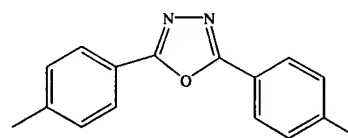
Ar	MW	mp °C	$\lambda_{\text{max}}(\text{abs})$ (nm)	$\lambda_{\text{max}}(\text{em})$ (nm)	ϕ_{em}	$\Delta E(\text{uv})$ (eV)
2.1	1110	198-220	350	398,416	0.93	3.11
2.2	954	222-232	382	442	0.39	2.87
2.3	998	235-258	347	393,410	1.08	3.19
---	778	230-235	334	416	0.93	3.08



2.1

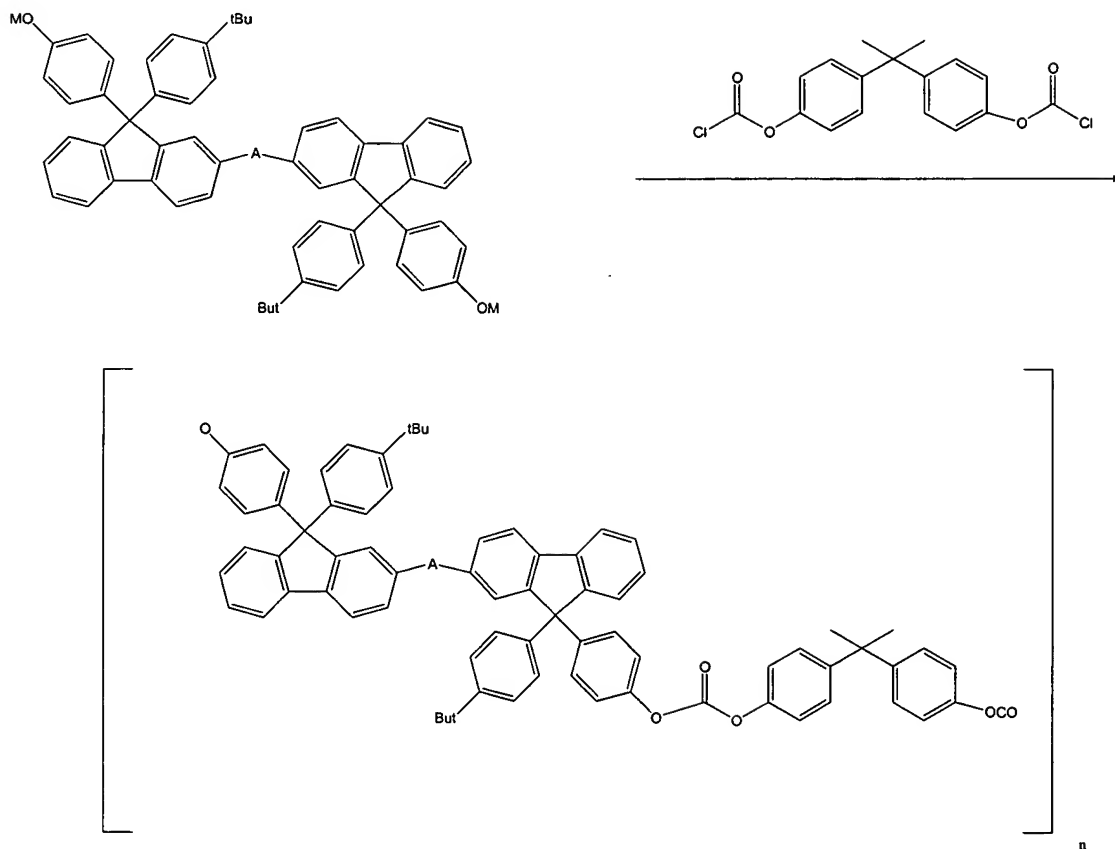


2.2



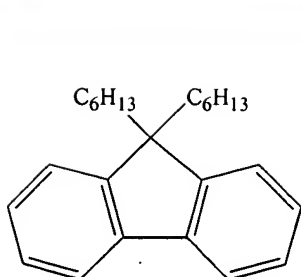
2.3

[00035] Table 3. Polymers

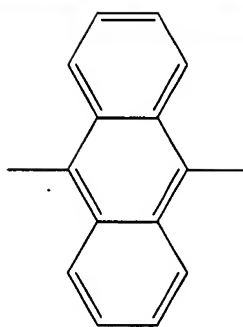


[00036]

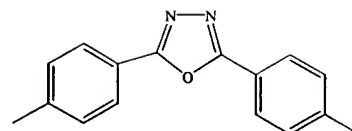
Ar	MW	Mn	$\lambda_{\max}(\text{abs})$ (nm)	$\lambda_{\max}(\text{em})$ (nm)	ϕ_{em}	$\Delta E(\text{uv})$ (eV)
3.1	20,098	8464	354	398,416	0.86	3.14
3.2	31,942	13,420	383,399	439	0.39	2.86
3.3	28,547	12,309	347	393,410	1.06	3.19
---	42,917	9307	333	387	-	3.35



3.1

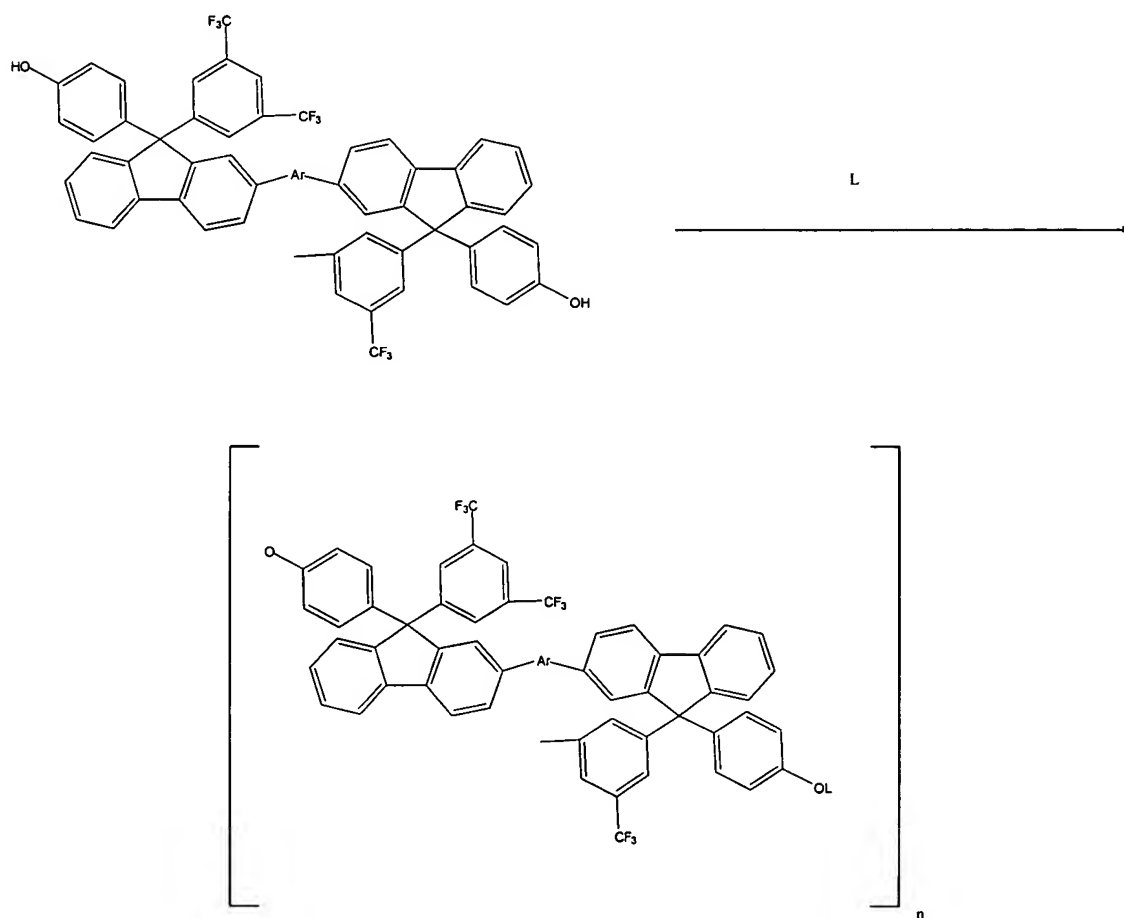


3.2

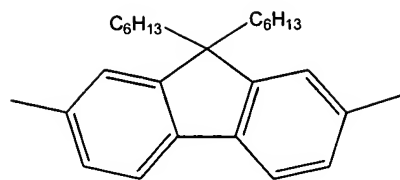


3.3

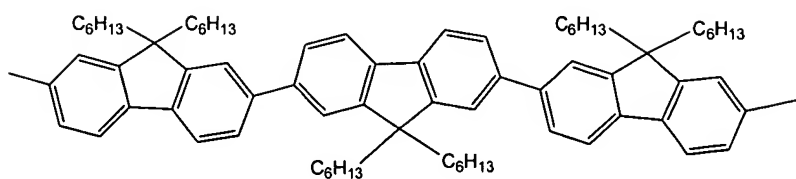
[00037] Additionally, several polymers were prepared according to the following scheme:



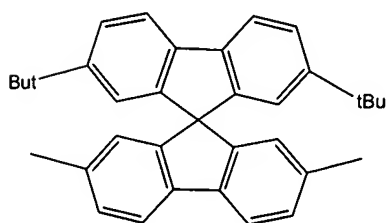
wherein Ar is:



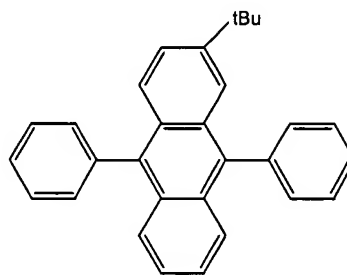
4.1



4.2

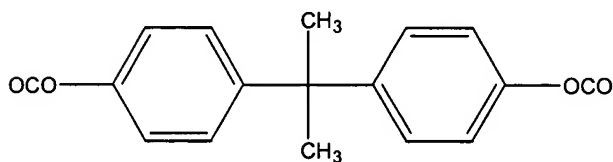


4.3

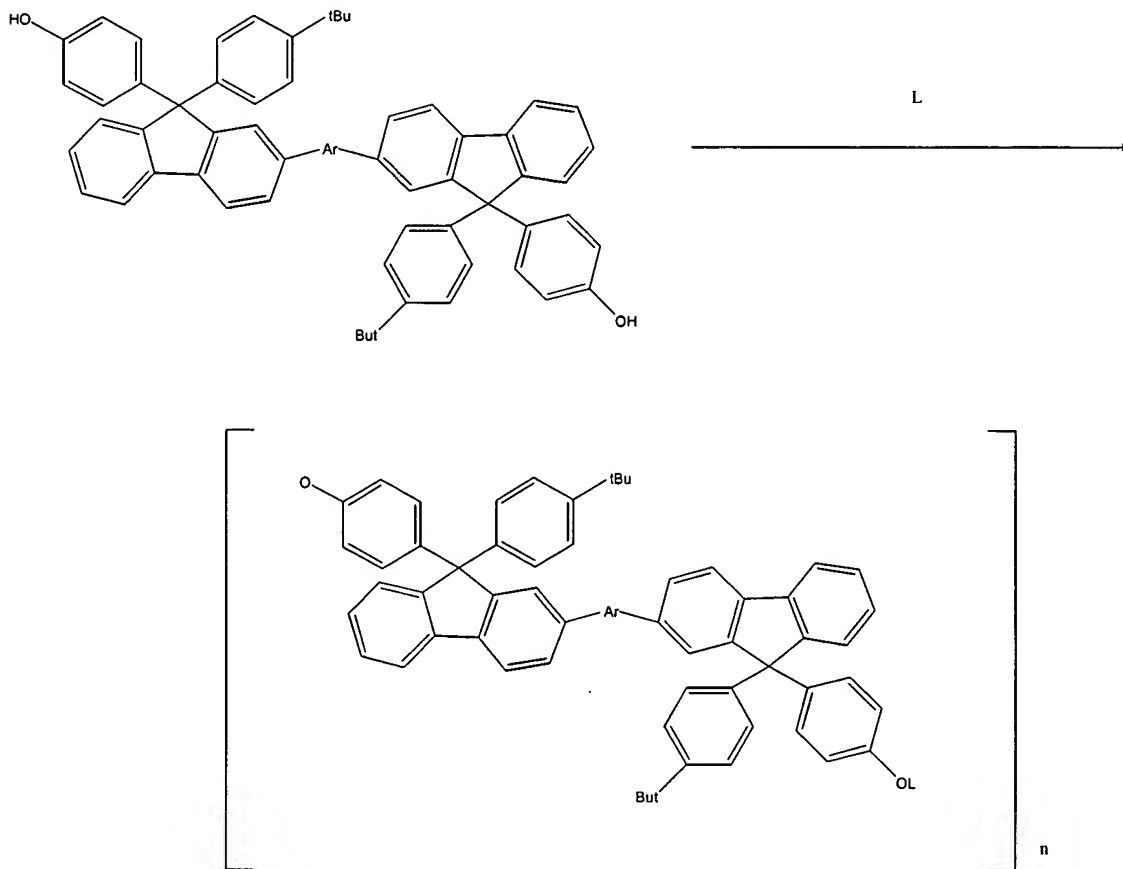


4.4

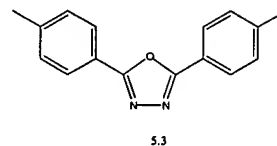
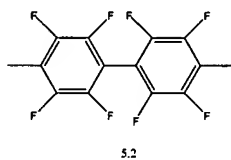
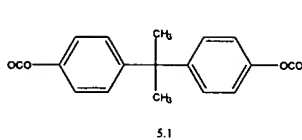
and L is:



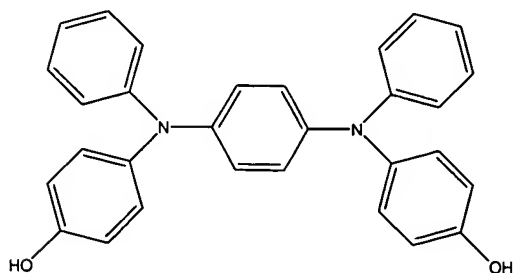
[00038] Polymers were also prepared according to the following scheme:



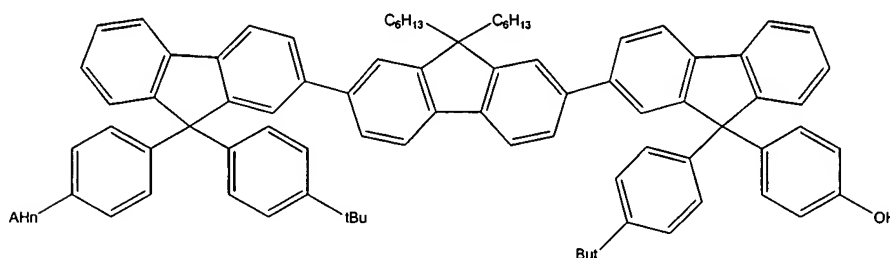
wherein Ar is the same as 2.1 previously set forth herein, and L is:



[00039] Additionally, with respect to the foregoing scheme, a polymer was formed using a co-monomer and structure 4.1. The co-monomer had the following structure:



[00040] Several polymers were prepared and tested in a device having the layered structure ITO/PEDOT/X/LiF/Al where X is the polymer according to the invention. The X polymer was prepared by reacting on oligomer of the formula:



with a difunctional monomer as defined in the Table 4 below.

[00041] Table 4. Device Data

Difunctional Monomer	Turn on V	W/W @20mA /cm ²	LPWr	CIE _x	CIE _y
Homo-PC	6.05	0.062%	229	0.222	0.297
Co-BPA PC	6.9	0.019%	170	0.208	0.228
Alt-BPA PC		-	-	-	-
Diphenylsilylether	5.4	.025%	335	0.176	0.143
CDTF1	3.11	0.23	130	0.173	0.138

[00042] In table 4, turn on V is the voltage at which the device emits visible light, W/W@20mA/cm², LPWr is lumens per watt, CIE_x and CIE_y are coordinates describing the color of the emitted light.

[00043] While the invention has been described herein relative to its preferred embodiments, it is of course contemplated that modifications of, and alternatives to, these embodiments, such modifications and alternatives obtaining the advantages and benefits of this invention, will be apparent to those of ordinary skill in the art having reference to this specification. It is contemplated that such modifications and alternatives are within the scope of this invention as subsequently claimed herein.